

## 9.10: Bonding in Metals

### Learning Objectives

- Explain the fundamental difference between the bonding in metallic solids compared to that in other types of solids and within molecules. Name some physical properties of metals that reflect this difference.
- Sketch out a diagram illustrating how a simple molecular-orbital approach to bonding in metals of Groups 1 and 2 always leaves some upper MO's empty.
- Describe, at the simplest level, the origin of electron "bands" in metals.
- Describe how the electrical and thermal conductivity of metals can be explained according to band theory.
- Explain why the electrical conductivity of a metal decreases with temperature, whereas that of a semiconductor increases.

Most of the known chemical elements are metals, and many of these combine with each other to form a large number of *intermetallic compounds*. The special properties of metals— their bright, lustrous appearance, their high electrical and thermal conductivities, and their malleability— suggest that these substances are bound together in a very special way.

### Properties of metals

The fact that the metallic elements are found on the left side of the periodic table offers an important clue to the nature of how they bond together to form solids.

- These elements all possess *low electronegativities* and readily form positive ions  $M^{n+}$ . Because they show no tendency to form negative ions, the kind of bonding present in ionic solids can immediately be ruled out.
- The metallic elements have empty or nearly-empty outer *p*-orbitals, so there are never enough outer-shell electrons to place an octet around an atom.

These points lead us to the simplest picture of metals, which regards them as a lattice of positive ions immersed in a “sea of electrons” which can freely migrate throughout the solid. In effect the electropositive nature of the metallic atoms allows their valence electrons to exist as a mobile fluid which can be displaced by an applied electric field, hence giving rise to their high *electrical conductivities*. Because each ion is surrounded by the electron fluid in all directions, the bonding has no directional properties; this accounts for the high *malleability* and *ductility* of metals.

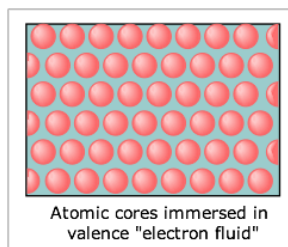


Figure 9.10.1: Atomic Cores Immersed in a Valence "Electron Fluid"

This view is an oversimplification that fails to explain metals in a quantitative way, nor can it account for the differences in the properties of individual metals. A more detailed treatment, known as the bond theory of metals, applies the idea of resonance hybrids to metallic lattices. In the case of an alkali metal, for example, this would involve a large number of hybrid structures in which a given Na atom shares its electron with its various neighbors.

### Molecular orbitals in metals

will look. These are all constructed by combining the individual atomic MO's that are so closely spaced in energy that they form what is known as a *band* of allowed energies. In metallic lithium only the lower half of this band is occupied.

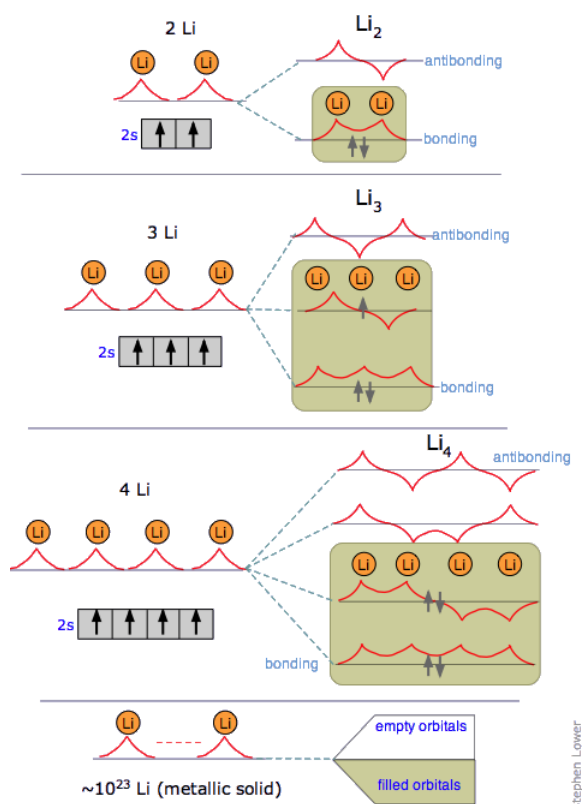


Figure 9.10.2: molecular orbitals in lithium molecules

## Origin of Metallic Properties

Metallic solids possess special properties that set them apart from other classes of solids and make them easy to identify and familiar to everyone. All of these properties derive from the liberation of the valence electrons from the control of individual atoms, allowing them to behave as a highly mobile fluid that fills the entire crystal lattice. What were previously valence-shell orbitals of individual atoms become split into huge numbers of closely-spaced levels known as bands that extend throughout the crystal.

## Melting Point and Strength

The strength of a metal derives from the electrostatic attraction between the lattice of positive ions and the fluid of valence electrons in which they are immersed. The larger the nuclear charge (atomic number) of the atomic kernel and the smaller its size, the greater this attraction. As with many other periodic properties, these work in opposite ways, as is seen by comparing the melting points of some of the Group 1-3 metals (right). Other factors, particularly the lattice geometry are also important, so exceptions such as is seen in Mg are not surprising.

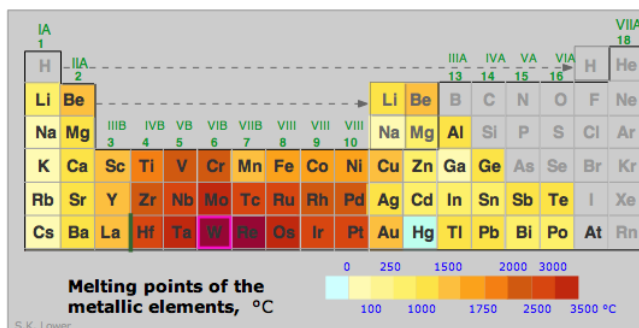


Figure 9.10.3: melting points of metals

In general, the transition metals with their valence-level  $d$  electrons are stronger and have higher melting points: Fe, 1539°C; Re 3180, Os 2727; W 3380°C.

## Malleability and ductility

These terms refer respectively to how readily a solid can be shaped by pressure (forging, hammering, rolling into a sheet) and by being drawn out into a wire. Metallic solids are known and valued for these qualities, which derive from the non-directional nature of the attractions between the kernel atoms and the electron fluid. The bonding within ionic or covalent solids may be stronger, but it is also directional, making these solids subject to fracture (brittle) when struck with a hammer, for example. A metal, by contrast, is more likely to be simply deformed or dented.

## Electrical conductivity: why are metals good conductors?

In order for a substance to conduct electricity, it must contain charged particles (*charge carriers*) that are sufficiently mobile to move in response to an applied electric field. In the case of ionic solutions and melts, the ions themselves serve this function. (Ionic solids contain the same charge carriers, but because they are fixed in place, these solids are insulators.) In metals the charge carriers are the electrons, and because they move freely through the lattice, metals are highly conductive. The very low mass and inertia of the electrons allows them to conduct high-frequency alternating currents, something that electrolytic solutions are incapable of. In terms of the band structure, application of an external field simply raises some of the electrons to previously unoccupied levels which possess greater momentum.

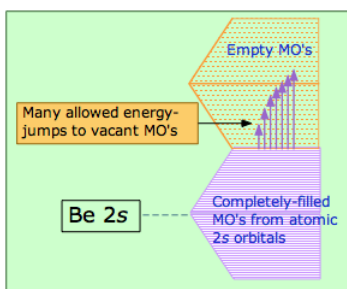


Figure 9.10.4: origin of metal conductivity

The conductivity of an electrolytic solution **decreases** as the temperature **falls** due to the decrease in "viscosity" which inhibits ionic mobility. The mobility of the electron fluid in metals is practically unaffected by temperature, but metals do suffer a slight conductivity decrease (opposite to ionic solutions) as the temperature rises; this happens because the more vigorous thermal motions of the kernel ions disrupts the uniform lattice structure that is required for free motion of the electrons within the crystal. Silver is the most conductive metal, followed by copper, gold, and aluminum.

Metals conduct electricity readily because of the essentially infinite supply of higher-energy empty MOs that electrons can populate as they acquire higher kinetic energies. This diagram illustrates the overlapping band structure (explained farther on) in beryllium. The MO levels are so closely spaced that even thermal energies can provide excitation and cause heat to rapidly spread through the solid.

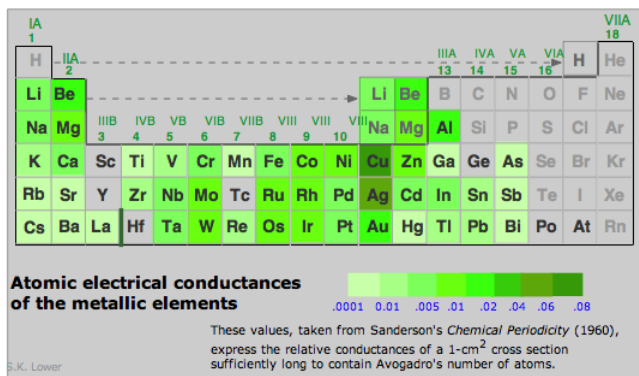


Figure 9.10.5: Electrical Conductances of the metals

Electrical conductivities of the metallic elements vary over a wide range. Notice that those of silver and copper (the highest of any metal) are in classes by themselves. Gold and aluminum follow close behind.

### Thermal conductivity: why do metals conduct heat?

Everyone knows that touching a metallic surface at room temperature produces a colder sensation than touching a piece of wood or plastic at the same temperature. The very high thermal conductivity of metals allows them to draw heat out of our bodies very efficiently if they are below body temperature. In the same way, a metallic surface that is above body temperature will feel much warmer than one made of some other material. The high thermal conductivity of metals is attributed to vibrational excitations of the fluid-like electrons; this excitation spreads through the crystal far more rapidly than it does in non-metallic solids which depend on vibrational motions of atoms which are much heavier and possess greater inertia.

### Appearance: Why are metals shiny?

We usually recognize a metal by its “metallic luster”, which refers to its ability to reflect light. When light falls on a metal, its rapidly changing electromagnetic field induces similar motions in the more loosely-bound electrons near the surface (this could not happen if the electrons were confined to the atomic valence shells.) A vibrating charge is itself an emitter of electromagnetic radiation, so the effect is to cause the metal to re-emit, or *reflect*, the incident light, producing the shiny appearance. What color is a metal? With the two exceptions of copper and gold, the closely-spaced levels in the bands allow metals to absorb all wavelengths equally well, so most metals are basically black, but this is ordinarily evident only when the metallic particles are so small that the band structure is not established.

The distinctive color of gold is a consequence of Einstein's theory of special relativity acting on the extremely high momentum of the inner-shell electrons, increasing their mass and causing the orbitals to contract. The outer (5d) electrons are less affected, and this gives rise to increased blue-light absorption, resulting in enhanced reflection of yellow and red light.

### Thermionic Effect

The electrons within the electron fluid have a distribution of velocities very much like that of molecules in a gas. When a metal is heated sufficiently, a fraction of these electrons will acquire sufficient kinetic energy to escape the metal altogether; some of the electrons are essentially “boiled out” of the metal. This *thermionic effect*, which was first observed by Thomas Edison, was utilized in vacuum tubes which served as the basis of electronics from its beginning around 1910 until semiconductors became dominant in the 1960's.

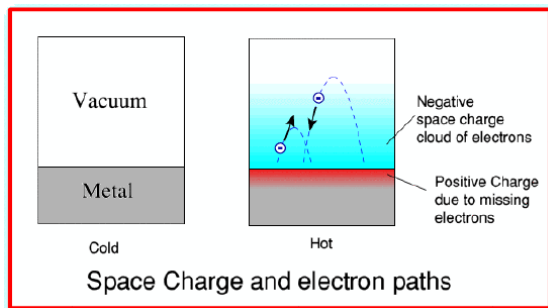


Figure 9.10.6: The Thermionic Effect

### Band Structure of Metals

Most metals are made of atoms that have an outer configuration of  $s^2$ , which we would expect to completely fill the band of MO's we have described. With the band completely filled and no empty levels above, we would not expect elements such as beryllium to be metallic. What happens is that the empty  $p$  orbitals also split into a band. Although the energy of the  $2p$  orbital of an isolated Be atom is about 160 kJ greater than that of the  $2s$  orbital, the bottom part of the  $2p$  band overlaps the upper part of the  $2s$  band, yielding a continuous *conduction band* that has plenty of unoccupied orbitals. It is only when these bands become filled with  $2p$  electrons that the elements lose their metallic character.

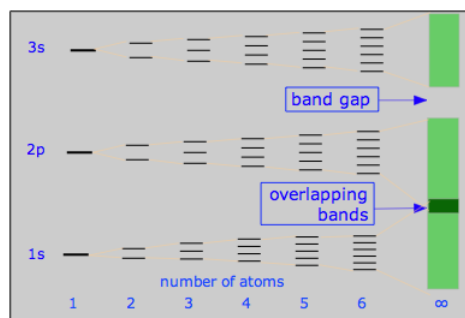


Figure 9.10.7: Origin of metal band structures

This diagram illustrates the band structure in a 3<sup>rd</sup>-row metal such as Na or Mg, and how it arises from MO splitting in very small units  $M_2$  -  $M_6$ . The conduction bands for the "infinite" molecule  $M_N$  are shaded.

In most metals there will be bands derived from the outermost *s*-, *p*-, and *d* atomic levels, leading to a system of bands, some of which will overlap as described above. Where overlap does not occur, the almost continuous energy levels of the bands are separated by a forbidden zone, or *band gap*. Only the outermost atomic orbitals form bands; the inner orbitals remain localized on the individual atoms and are not involved in bonding.

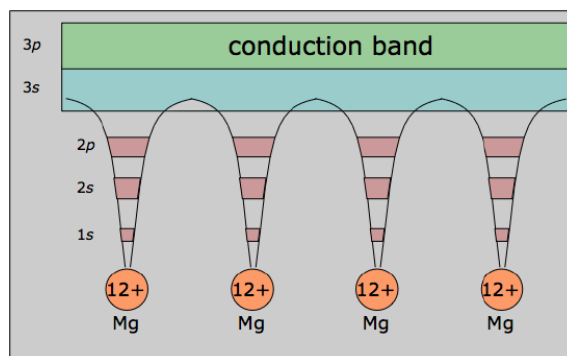


Figure 9.10.8: Conduction Bands in Magnesium solids

In its mathematical development, the band model relies strongly on the way that the free electrons within the metal interact with the ordered regularity of the crystal lattice. The alternative view shown here emphasizes this aspect by showing the inner orbitals as localized to the atomic cores, while the valence electrons are delocalized and belong to the metal as a whole, which in a sense constitutes a huge molecule in its own right.

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